Thermodynamic modelling of aqueous aerosols containing electrolytes and dissolved organic compounds

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Abstract

A method for calculating the thermodynamic properties of soluble mixed inorganic/organic aerosols is proposed. It is based upon the use of existing models of inorganic (electrolyte) multicomponent solutions and water/organic mixtures in combination, together with simple thermodynamically consistent terms that express the effects of interactions between ions and organic molecules on the activities of all mixture components. The method is used to calculate the deliquescence properties of the following systems at 298.15 K: sodium chloride/sucrose/water, letovicite/2-butenedioic acid/water, and sodium chloride/butanoic acid/water. The effects of approximations in the ion–organic interaction terms are explored, and it is shown that the method can be used to model liquid/liquid phase separation in sodium chloride/butanoic acid/water mixtures. In this example, it is found that the phase separation results in total water uptake that differs little from that of pure sodium chloride. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Aqueous aerosols; Thermodynamics; Activity coefficients; Electrolytes; Soluble organic compounds

1. Introduction

Many urban and background tropospheric aerosols contain large fractions of soluble organic material (e.g., Malm, Sisler, Auffman, Eldred, & Cahill, 1994), which is derived in part from the oxidation of anthropogenic hydrocarbons and other gas-phase precursors such as the monoterpenes

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(Hoffmann et al., 1997; Decesari, Facchini, Fuzzi, & Tagliavini, 2000). The organic component of the aerosol will affect the water uptake and deliquescence properties, thus influencing aerosol size (Saxena, Hildemann, McMurry, & Seinfeld, 1995). Organic aerosols also may function as cloud condensation nuclei (Novakov & Penner, 1993).

The chemical composition of aerosol organic matter is complex and not yet fully understood, although for some aerosols the functional groups present have been measured (Blando et al., 1998) and individual compounds identified in laboratory oxidation experiments for simple systems (Yu, Cocker, Griffin, Flagan, & Seinfeld, 1999). The key properties of soluble inorganic aerosols — water uptake, deliquescence of the salts present, and equilibrium with gases such as NH_3 and HNO_3 — usually are calculated using thermodynamic models (Zhang et al., 2000). These models predict values of the activities of water and the dissolved ions in the liquid aerosol droplets, which are used together with equilibrium constants to determine the physical state and composition of the aerosol under ambient conditions. It clearly is desirable to extend these models to include soluble organic compounds and so treat internally mixed inorganic/organic aerosols. However, there are two main difficulties. First is the lack of fundamental thermodynamic data for organic compounds. Such data include Henry's law constants, equilibrium vapour pressures of water/organic mixtures as a function of solution composition, the pK_as of organic compounds that are weak acids and the solubilities of their salts. Second, a suitable theoretical approach must be found which allows the properties of soluble aerosols including organic components to be predicted, despite the complex aerosol composition and sparse thermodynamic data.

We propose a practical approach for calculating the properties of soluble mixed inorganic/organic aerosols. This involves the use of existing models of inorganic solutions and water/organic mixtures, combined with a self-consistent method of incorporating the mutual influence of ions and organic molecules on the activities of all components.

2. Theory

2.1. Background

Thermodynamic models of aqueous inorganic mixtures are relatively well developed, and those applied in aerosol science (Zhang et al., 2000) may broadly be characterised as based upon either mixing rules or ion interaction equations. Examples of the former include the Kusik and Meissner (1978) method. The Zdanovski–Stokes–Robinson rule (Stokes & Robinson, 1966) is commonly used to estimate solution molality for a specified water activity. The two principal ion interaction models in use are the Pitzer molality-based model (Pitzer, 1991) and the Pitzer–Simonson–Clegg mole fraction model (Clegg, Pitzer, & Brimblecombe, 1992).

The Zdanovski–Stokes–Robinson method can in principle be applied to aqueous aerosols containing dissolved organic compounds, as it requires only values of the molalities of the various single salt solutions, and/or single organic compound solutions, at a specified water activity to calculate the overall concentration of the mixture. However, neither the Kusik and Meissner method nor other models, such as that of Bromley (1973), can be used readily to estimate the activities of neutral (uncharged) species such as organic molecules in mixed solutions containing electrolytes.

The Pitzer–Simonson–Clegg model has been developed to include neutral solutes as solution components. However, it is difficult to apply in that form to problems in aerosol chemistry as the presence of neutral species leads to the liquid mixture being treated as a mixed solvent system. This necessitates the correction of calculated ionic activity coefficients to a reference state of infinite dilution in pure water (or the correction of all equilibrium constants involving ions to a reference state of infinite dilution in the mixed solvent). Even a relatively simple and approximate method of doing this such as the Born equation (e.g., Austgen, Rochelle, Peng, & Chen, 1989) requires data for the pure organic components that are unlikely to be available. The Pitzer molality-based equations incorporate uncharged solutes without any need for reference state corrections. However, the very high liquid phase concentrations that are attained at low relative humidities (water activities) can lead to unstable behaviour and generally poor predictions.

The larger problem for both models above, and indeed for most calculations, is the requirement for thermodynamic data from which the interactions between water and organic solutes, and organic solutes and ions, can be determined. Fundamental properties such as the vapour pressures of the secondary organic aerosol compounds likely to partition into aerosols have not been measured. Some data exist for the salt effect on the solubilities of organic vapours in water, but mostly for very simple compounds only (Long & McDevit, 1952).

2.2. The model

A model of soluble aerosols containing water and inorganic and organic components should have the following properties. First, for the two limiting cases of an aqueous electrolyte solution, and a mixture of organic compounds in water, it should yield results as accurate as existing models. Second, the effect on aerosol solution behaviour of the interaction of dissolved ions and organic molecules should be included, allowing varying levels of complexity in the way that these interactions are represented. This is necessary as few thermodynamic data are available currently for many aqueous ion/organic mixtures of relevance.

The general problem — that of predicting the activities of all species in ion/organic/water solutions for all possible compositions — would require a complex model and an unrealistically large amount of data for the various compounds present and their mixtures. We distinguish two different cases: (i) that in which the concentrations of organic molecules in the liquid phase are sufficiently low that water can be considered the solvent; (ii) that in which the organic compounds are present in amounts similar to, or larger than, water itself. The latter case is likely to occur at low atmospheric relative humidities for aerosols with a large soluble organic fraction.

In the second case it is both physically unrealistic and impractical to treat the liquid mixture as consisting of ions and organic molecules dissolved in a water solvent. While the thermodynamics of liquid mixtures of water and organic compounds can be estimated using methods such as UNIQUAC and UNIFAC (Abrams & Prausnitz, 1975; Fredenslund, Jones, & Prausnitz, 1975), there are considerable problems in predicting the properties of such mixed solvent systems containing high concentrations of dissolved electrolytes. Because of this, it is likely that different approaches will be necessary for the two cases. In this work we deal only with case (i), which is considered below.

First, we assume that the mean activity coefficient of an electrolyte $M_{v+}X_{v-}$ in a solution containing both the electrolyte and uncharged molecular solute can be expressed as the logarithm

of the activity coefficient of $M_{v+}X_{v-}$ in a pure solution of $M_{v+}X_{v-}$ at its molality in the mixture, plus further terms in the molalities of M^{z+}, X^{z-} and the molecular solute multiplied together. The analogous relationship also is true for the activity coefficient of the molecular solute. This statement can be further generalised to an arbitrarily complex solution: the activity coefficient of a cation or anion can be expressed as the logarithm of its activity coefficient in a solution containing all the ions only (at their molalities in the mixture), plus additional terms in the molalities of ions and molecular solutes. The analogous relationship also is again true for molecular solutes. The formulation of the Pitzer equations (Pitzer, 1991) is consistent with this view.

Second, the purely ionic contributions to a molality-based activity coefficient, and those arising only from molecular solutes, are expressed independently of one another and therefore need not be calculated using the same model. This key element of our approach enables different models for ionic and molecular (organic) components of a solution to be combined in a self-consistent way to estimate the properties of the mixture. The method is now described.

The molal activity coefficients of an ion (γ_i) and an uncharged organic solute (γ_n) in a liquid mixture are given as follows:

$$\ln(\gamma_i) = \Delta \ln(\gamma_i[\text{ion–water}]) + \Delta \ln(\gamma_j[\text{ion–organic}]), \tag{1a}$$

$$\ln(\gamma_n) = \Delta \ln(\gamma_n[\text{organic–water}]) + \Delta \ln(\gamma_n[\text{ion–organic}]), \tag{1b}$$

where each Δ element is a contribution to the activity coefficient resulting from ion–water, organic compound–water, or ion–organic compound terms, which are calculated independently. Eq. (1) can be considered analogous to the ion-interaction model of Pitzer (1991) in which equations for activity coefficients are composed of summations of terms for binary and ternary interactions between different species, which are then summed. The Δ terms in Eq. (1) are

$$\Delta \ln(\gamma_i[\text{ion–water}]) = \ln(\gamma_i') = \ln(f_i^{*\prime}) + \ln(x_w'), \tag{2a}$$

$$\Delta \ln(\gamma_n[\text{organic–water}]) = \ln(\gamma_n'') = \ln(f_n^{*\prime\prime}) + \ln(x_w''), \tag{2b}$$

$$\Delta \ln(\gamma_j[\text{ion–organic}]) = \ln(\gamma_j''). \tag{2c}$$

In Eq. (2a) species i is an ion, in Eq. (2b) n is an uncharged (generally organic) molecule, and in Eq. (2c) j can be either an ion or organic molecule. Thus, the contributions to the activity coefficient of ion i in Eq. (1a) are from Eqs. (2a) and (2c) only, and for the activity coefficient of molecular solute n in Eq. (1b) there are contributions from Eqs. (2b) and (2c) only. It is likely that for many systems the ion–water and organic–water terms in Eqs. (2a) and (2b) will be calculated using a mole fraction based model, thus yielding activity coefficients $f_n^{*\prime}$ and $f_n^{*\prime\prime}$ on the same scale. This gives rise to the two adjustment terms in the pseudo-mole fractions of water (x_w' and x_w''), which are required to convert the mole fraction activity coefficients to a molality basis. The mole fractions are calculated either from the amounts of water and ions only (x_w'), or from the amounts of water and uncharged organic solutes only (x_w'').

The corresponding relationship to Eq. (2) for the water activity is defined in terms of the osmotic coefficient of the solution, ϕ:

$$\phi - 1 = (\phi' - 1)\left(\sum_i m_i\right)\bigg/\left(\sum_j m_j\right) + (\phi'' - 1)\left(\sum_n m_n\right)\bigg/\left(\sum_j m_j\right) + (\phi''' - 1), \tag{3}$$

where ϕ' is the osmotic coefficient contribution from the ionic components of the solution, ϕ'' is the contribution from molecular solutes, and ϕ''' is the contribution from ion-organic interactions. The summations are over the molalities m_i of solute ions i, the molalities m_n of uncharged solute molecules n, and molalities m_j of all solute species (ions and molecules). These definitions apply in all the equations presented in this work. In applications of Eq. (3) where one of the osmotic coefficients is not calculated it is assumed to have a value of unity so that the net contribution to $(\phi - 1)$ is zero.

The osmotic coefficient ϕ is related to the water activity of the solution, a_w, by the expression $\ln(a_w) = -M_w \phi \sum_j m_j$, where M_w is the molar mass of the solvent water (0.0180152 kg mol^{-1}).

The activity and osmotic coefficient contributions on the right-hand sides of Eqs. (2a), (2b) and (3) are calculated using models for "partial" compositions of the solution, neglecting uncharged molecules in Eq. (2a) and ions in Eq. (2b). The calculation of these terms is described next.

(a) *Ion–water interactions*: The terms $\Delta \ln(\gamma_i[\text{ion–water}])$ and $(\phi' - 1)$ contribute only to the activity coefficients of dissolved ions and the osmotic coefficient of water. For all mixture compositions the terms are calculated using a partial, or pseudo, composition that neglects the organic component. If a mole fraction model is used for this purpose, then pseudo-mole fractions x_i' are used as concentration variables

$$x_i' = n_i \bigg/ \left(n_w + \sum_i n_i \right), \tag{4}$$

where n_i is the number of moles of ion i, and n_w the number of moles of the solvent, water. The same expression is applied to water, in which case $x_w' = n_w/(n_w + \sum_i n_i)$. Neglect of the organic components of the liquid mixture does not affect ion molalities.

Consider a mixture consisting of 55.51 mol of H_2O (1 kg), 4 mol of NaCl, and 20 mol of some organic compound N. The molality of NaCl in the mixture for pure water solvent is 4 mol kg^{-1}, and the mole fractions of Na$^+$ and Cl$^-$ are $x_{Na} = x_{Cl} = 4/(4 + 4 + 55.51 + 20) = 0.04790$. The pseudo-mole fractions are $x_{Na}' = x_{Cl}' = 4/(4 + 4 + 55.51) = 0.06298$, and $x_w' = 55.51/(4 + 4 + 55.51) = 0.87404$. The ion–water contributions to the osmotic coefficient of water, and activity coefficients Na$^+$ and Cl$^-$, are obtained by first calculating values for 4 mol kg^{-1} (or $x_{Na}', x_{Cl}' = 0.06298$) pure aqueous NaCl. For example, at 298.15 K, the water activity of aqueous NaCl at this molality is 0.8514 (Hamer & Wu, 1972) yielding an osmotic coefficient contribution (ϕ') equal to $-\ln(0.8514)/(0.0180152 \times 2 \times 4) = 0.5581$. The contribution of the ion–water interaction to the true osmotic coefficient of water (ϕ) in the mixture is then $0.5581 \times (4 + 4)/(4 + 4 + 20)$, as given by the first term in Eq. (3).

For a liquid mixture containing several ions the ion activity or osmotic coefficient contributions are estimated with a model using either the ionic molalities or pseudo mole fractions.

(b) *Organic–water interactions*: The terms $\Delta \ln(\gamma_n[\text{organic–water}])$ and $(\phi'' - 1)$ contribute only to the activity coefficients of organic molecules in the mixture and the osmotic coefficient and are zero for all ions. The terms are calculated for compositions neglecting the ions in the liquid mixture. Thus, we define a second set of pseudo-mole fractions x_n'' by

$$x_n'' = n_n \bigg/ \left(n_w + \sum_n n_n \right), \tag{5}$$

where n_n is the number of moles of organic molecule n. For water $x''_w = n_w/(n_w + \sum_n n_n)$. In models for calculating the organic–water contributions to thermodynamic properties, such as UNIFAC, the reference state for activity coefficients is the pure liquid for each component. Thus, $f''_n \to 1$ as $x''_n \to 1$; consequently, each component has unit activity as a pure liquid. Conversion to the same reference state as the ions ($f^{*''}_i \to 1$ as $x''_w \to 1$) can be carried out without difficulty (see Robinson & Stokes, 1965).

For the example in subsection (a) above, the pseudo-mole fraction of N, x''_N, is equal to $20/(55.51 + 20) = 0.26487$ and that of water (x''_w) is $55.51/(55.51 + 20) = 0.73513$. If compound N is ethanol (eth) we find that UNIFAC yields an activity coefficient $\ln(f^{*''}_{eth}) = -1.4626$ at 298.15 K, and $\phi'' = 0.3582$ from a water activity of 0.8789 for the ethanol–water mixture. The organic–water contribution to the logarithm of the ethanol activity coefficient in the NaCl/water/ethanol mixture is then given by $-1.4626 + \ln(0.73513) = -1.7703$ (Eq. (2b)).

(c) *Ion–organic interactions*: These terms $\Delta\ln(\gamma_j[\text{ion–organic}])$ and $(\phi''' - 1)$ contribute to the osmotic coefficient and activity coefficients of all solutes. For thermodynamic consistency, they should be derived from a single expression for the ion–organic contribution to the excess Gibbs energy of the solution (e.g., Pitzer, 1991).

As an example we give two of the principal ion–organic interaction terms that occur in the Pitzer molality-based model (Clegg & Whitfield, 1991):

$$G^{ex'''}/w_w RT = 2\sum_n \sum_i m_n m_i \lambda_{ni} + \sum_n \sum_c \sum_a m_n m_c m_a \zeta_{nca}, \tag{6}$$

$$\ln(\gamma'''_i) = 2\sum_n m_n \lambda_{ni} + \sum_n \sum_k m_n m_k \zeta_{nik}, \tag{7a}$$

$$\ln(\gamma'''_N) = 2\sum_i m_i \lambda_{Ni} + \sum_c \sum_a m_c m_a \zeta_{Nca}, \tag{7b}$$

$$\phi''' - 1 = \left(2\Big/\sum_j m_j\right)\left[\sum_n \sum_i m_n m_i \lambda_{ni} + \sum_n \sum_c \sum_a m_n m_c m_a \zeta_{nca}\right]. \tag{7c}$$

The summations in c and a are over all cations and anions, respectively. In Eq. (7a) summation k is over all ions of opposite charge type to the primary ion i. Summations over i and j are as previously defined.

The unknown model parameters in the above expressions (λ_{ni} and ζ_{nca}) are usually determined from solubility, partitioning, and calorimetric data over the temperature range of interest (e.g., Clegg & Brimblecombe, 1989; 1990). However, comprehensive measurements are necessary to obtain both parameters, and others that might apply, and for many organic molecules such a complex treatment is not possible. However, the expressions above have proved useful for modelling oxygen and ammonia solubilities for which accurate data are available (see the references above).

The Setchenow rule expresses the simplest observed behaviour of organic compound solubilities in salt solutions (Harned & Owen, 1958; Clegg & Whitfield, 1991). It is given by

$$\ln(S^0/S) = kc_s, \tag{8}$$

where S is the solubility of the organic or other uncharged solute in a solution containing salt 's', S^0 is the solubility in pure water, c_s is the concentration (molarity) of the salt solution, and k is an experimentally determined proportionality constant. The quantity S^0/S is equivalent to the molar activity coefficient of the organic species. Values of k are listed for many simple organic compounds in reviews such as those of Randall and Failey (1927a,b), Long and McDevit (1952), and the IUPAC Solubility Data Series (IUPAC, 1979-present). The terms in Eqs. (7a)–(7c) corresponding to the Setchenow rule on a molality basis are those involving the interaction parameter λ_{ni}. Because of the constraint of electroneutrality, values of individual ion–organic interaction parameters λ_{ni} cannot be determined. However, for an organic compound N dissolved in aqueous solution containing a single salt $M_{v+}X_{v-}$ Eq. (7b) can be written

$$\ln(\gamma_N''') = 2m(v_+\lambda_{N,M} + v_-\lambda_{N,X}) + m^2(v_+v_-)\zeta_{N,M,X}, \tag{9}$$

where m is the molality of salt $M_{v+}X_{v-}$. Analogous relationships apply for Eqs. (7a) and (7c). Individual values of λ_{ni} and are obtained from the experimentally determined sums by arbitrarily setting to zero one λ_{nc} or λ_{na}. For example, when modelling CO_2 solubility Harvie, Moller, and Weare (1984) assigned $\lambda_{CO_2,H}$ to zero, while Clegg and Brimblecombe (1989) set $\lambda_{NH_3,Cl}$ to zero in their study of ammonia solubilities. This does not result in any thermodynamic inconsistency where cation and anion activities are used in combination, as they are in the calculation of chemical equilibria.

3. Practical applications

In Eq. (1) for the total activity coefficient of an ion or solute molecule, and Eq. (3) for the osmotic coefficient of the solution, the first terms are the contributions of ion–water interactions. These can be calculated using an existing mixing rule or ion-interaction model ignoring the dissolved organic content of the mixture, as described in Section 2.

The second terms in Eqs. (1) and (3) account for organic–water interactions. The UNIFAC model has been proposed as a method for calculating activity coefficients in aerosols containing water and organic compounds (Saxena & Hildemann, 1997), and can be used to calculate the organic–water term where experimental data are not available. In the UNIFAC model the behaviour of each compound is calculated from its functional group composition. It is certainly the case that UNIFAC is primarily intended for relatively simple compounds in which, for example, functional groups do not significantly interact with one another. UNIFAC does not involve any positional terms, and compounds that consist of the same functional groups — though they may be very differently arranged — have identical calculated activities. The structures of the compounds occurring in secondary organic aerosols are complex, the molecules being highly oxygenated. Comparisons of measured and predicted water activities of aqueous solutions of organic compounds have made it clear that UNIFAC is not an ideal tool (Saxena & Hildemann, 1997). However, other models that can be applied (except in limited cases) do not appear to exist, and in most instances the use of UNIFAC may be preferable to assuming $\Delta\ln(\gamma_j[\text{organic–water}])$ and $(\phi'' - 1) = 0$. This assumption should, however, be tested.

The last elements in Eqs. (1) and (3) are the ion–organic contributions, which can be expressed in terms of interaction parameters such as λ_{ni} whose values need to be estimated from solubility or

other data. It is important to assess the effects of these interactions on the thermodynamic properties of mixtures, and to determine the degree of accuracy to which the ion–organic interactions need be known to represent atmospherically important properties such as deliquescence behaviour, and also to establish the range of liquid-phase concentrations over which molality-based ion–organic interaction terms can be used.

Next, the modelling approach is applied to various test cases involving organic compounds and salts to address these questions. The first example involves a solution mixture for which comprehensive activity and solubility data are available. Here we examine the effect of using only a simple "salting coefficient" for ion–organic interactions, and neglecting ion–organic interactions altogether. This is done by comparing predicted deliquescence curves of the system, for various approximations in the thermodynamic model, with an accurate calculation based upon all the available data. In the second example, a more realistic atmospheric system is studied, involving an acidic salt and a dicarboxylic acid. Here we focus on uncertainties in the properties of aqueous solutions of the organic acid, and the influence on deliquescence properties of a range of possible values of the salting coefficient λ_{ni}. Last, a salt/organic acid/water mixture which shows liquid–liquid phase separation is modelled. Such behaviour is unique to systems containing organic compounds. The deliquescence properties of the mixture are calculated, and the atmospheric significance briefly discussed.

3.1. Sodium chloride/sucrose $(C_{12}H_{22}O_{11})$/water

This mixture is used as an example of the application of the model, and to assess the sensitivity of deliquescence properties to the ion–organic interactions and the accuracy to which they are parameterised. While $NaCl/C_{12}H_{22}O_{11}/H_2O$ has little direct atmospheric relevance, the thermodynamic properties of the system are unusually well characterised for all compositions and molalities up to the solubilities of $NaCl_{(s)}$ (6.144 mol kg^{-1} in pure aqueous NaCl; Hamer & Wu, 1972) and sucrose (approximately 6.19 mol kg^{-1} in pure aqueous sucrose; Stephen & Stephen, 1979a). Osmotic coefficients have been determined by Robinson, Stokes, and Marsh (1970), and emf measurements of NaCl activities have been made by Wang, Liu, Fan, and Lu (1994) for NaCl molalities up to 2 mol kg^{-1}. Both $NaCl_{(s)}$ and $C_{12}H_{22}O_{11(s)}$ solubilities in the solution mixtures are also available (Stephen & Stephen, 1979b; Hu & Guo, 1999). Stokes (1995) has presented equations that enable activity coefficients of both NaCl and $C_{12}H_{22}O_{11}$ in the mixture to be calculated. He has demonstrated that the measured activity coefficients of Wang et al. (1994) are consistent with the osmotic coefficients.

Water activities of the $NaCl/C_{12}H_{22}O_{11}/H_2O$ solutions are calculated from osmotic coefficients given by Eq. (3). Values of ϕ', the osmotic coefficient of pure aqueous NaCl at the molality of NaCl in the mixture, are here taken from Archer (1992). Osmotic coefficients of aqueous sucrose solutions at 298.15 K, ϕ'' in the model, are given by Eq. (C1) in Table 1 as a function of molality, m. The expression is valid up to the saturation molality of 6.19 mol kg^{-1}, and was derived by fitting to isopiestic data from Scatchard, Hamer, and Wood (1938) for pure aqueous sucrose, using osmotic coefficients of the reference solutions from recent reviews (Archer, 1992; 1999; Clegg, Rard, & Pitzer, 1994).

For most soluble aerosols containing both inorganic and organic components there are likely to be few, if any, data from which the mixture contribution ϕ''' to the total osmotic coefficient can be

Table 1
Equations for the properties of $NaCl/C_{12}H_{22}O_{11}/H_2O$ mixtures[a]

$$\phi'' - 1 = 0.0752676m + 0.0162273m^2 - 0.00364864m^3 + 2.01227 \times 10^{-4}m^4 \tag{C1}$$

$$\phi''' - 1 = [mNaCl \cdot mC_{12}H_{22}O_{11}/(2mNaCl + mC_{12}H_{22}O_{11})]$$
$$\times (b_0 + b_1 mNaCl + b_2 mC_{12}H_{22}O_{11} + b_3 mNaCl^2 + b_4 mC_{12}H_{22}O_{11}^2$$
$$+ b_5 mNaCl \cdot mC_{12}H_{22}O_{11} + b_6 mNaCl^2 \cdot mC_{12}H_{22}O_{11}) \tag{C2}$$

$$\ln(\gamma''_{NaCl}) = 0.5(b_0 mC_{12}H_{22}O_{11} + b_1 mNaCl \cdot mC_{12}H_{22}O_{11} + (1/2)b_2 mNaCl \cdot mC_{12}H_{22}O_{11}^2$$
$$+ b_3 mNaCl^2 \cdot mC_{12}H_{22}O_{11} + (1/3)b_4 mNaCl \cdot mC_{12}H_{22}O_{11}^3$$
$$+ (2/3)b_5 mNaCl \cdot mC_{12}H_{22}O_{11}^2 + (3/4)b_6 mNaCl^2 \cdot mC_{12}H_{22}O_{11}^2) \tag{C3}$$

$$\ln(\gamma''_{Sucr}) = 2 \times 0.0752676 \times mC_{12}H_{22}O_{11} + (3/2) \times 0.0162273 mC_{12}H_{22}O_{11}^2$$
$$- (4/3) \times 0.0162273 mC_{12}H_{22}O_{11}^3 + (5/4) \times 2.01227 \times 10^{-4} mC_{12}H_{22}O_{11}^4 \tag{C4}$$

$$\ln(\gamma'''_{Sucr}) = b_0 mNaCl + (1/2)b_1 mNaCl^2 + b_2 mNaCl \cdot mC_{12}H_{22}O_{11} + (1/3)b_3 mNaCl^3$$
$$+ b_4 mNaCl \cdot mC_{12}H_{22}O_{11}^2 + (2/3)b_5 mNaCl^2 \cdot mC_{12}H_{22}O_{11} + (1/2)b_6 mNaCl^3 \cdot mC_{12}H_{22}O_{11} \tag{C5}$$

$$\ln(\gamma_{Sucr}^{\infty}) = 2mNaCl \cdot \lambda_{Sucr,Na} + mNaCl^2 \cdot \zeta_{Sucr,Na,Cl} \tag{C6}$$

$$\phi''' - 1 = [2 /(2mNaCl + mC_{12}H_{22}O_{11})](mNaCl \cdot mC_{12}H_{22}O_{11} \cdot \lambda_{Sucr,Na} + mNaCl^2 \cdot mC_{12}H_{22}O_{11} \cdot \zeta_{Sucr,Na,Cl}) \tag{C7}$$

$$\ln(\gamma'''_{NaCl}) = 0.5(\ln(\gamma'''_{Na}) + \ln(\gamma'''_{Cl}))$$
$$= mC_{12}H_{22}O_{11} \cdot \lambda_{Sucr,Na} + mNaCl \cdot mC_{12}H_{22}O_{11} \cdot \zeta_{Sucr,Na,Cl} \tag{C8}$$

[a]Values of coefficients b_0 to b_6 in Eqs. (C1), (C2) and (C5) are as follows: b_0, 0.0926008; b_1, -0.015005; b_2, -0.00916286; b_3, -0.00193288; b_4, 3.51587×10^{-4}; b_5, -0.00268803; b_6, 5.56483×10^{-4}. Coefficients $\lambda_{Sucr,Na}$ and $\zeta_{Sucr,Na,Cl}$ in Eqs. (C6) to (C8) are equal to 0.0512 and -0.01279, respectively.

derived. However, for the present system it is possible to use the osmotic coefficients of Robinson et al. (1970) to determine ϕ''' to high accuracy, and so calculate a reference deliquescence curve for $NaCl/C_{12}H_{22}O_{11}/H_2O$ with which the predictions of simpler expressions can be compared. Taking Eq. (3), and subtracting the pure solution contributions to the total osmotic coefficient of the solution we follow Robinson et al. (1970) and Stokes (1995) and fit Eq. (C2) in Table 1 for $(\phi''' - 1)$. The combined equations represent the data within, or close to, the experimental uncertainty in the total osmotic coefficient ϕ.

The activity coefficients of the two solutes are required to calculate the precipitation of the solids $NaCl_{(s)}$ and $C_{12}H_{22}O_{11(s)}$ in the $NaCl/C_{12}H_{22}O_{11}/H_2O$ mixtures. The general expression for the mean molal activity coefficient of NaCl (γ_{NaCl}, equal to $(\gamma_{Na}\gamma_{Cl})^{1/2}$) in the mixture is given by Eqs. (1a) and (2). The value of $\ln(\gamma'_{NaCl})$, for a pure aqueous NaCl solution at the molality of NaCl in the mixture, is taken from Archer (1992). From the Gibbs–Duhem relation the expression for the ion–organic contribution (γ'''_{NaCl}) to the total mean activity coefficient of NaCl is given by Eq. (C3) in Table 1.

The pure aqueous solution contribution to the activity coefficient of $C_{12}H_{22}O_{11}$ (γ''_{Sucr}) can be obtained from Eq. (C1), and is given by Eq. (C4) in Table 1. There is no ion–water contribution to the activity coefficient of an organic molecule. The mixture contribution (γ'''_{Sucr}) to the total activity
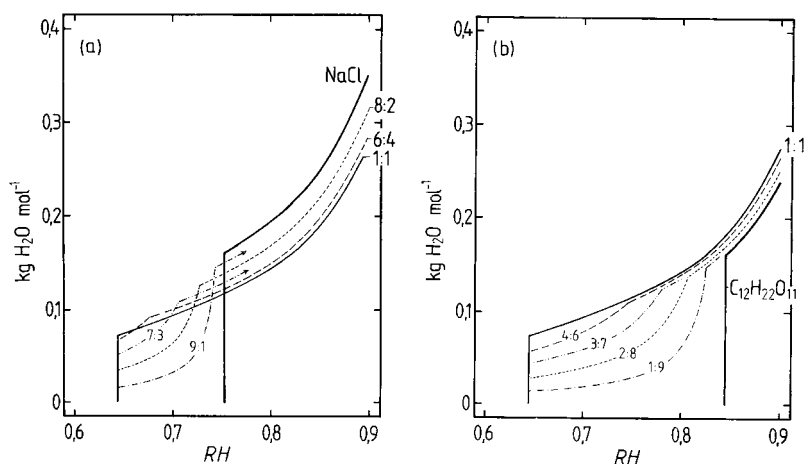
Fig. 1. Deliquescence curves for NaCl/$C_{12}H_{22}O_{11}$ (sucrose) mixtures at 298.15 K, calculated using the full model parameterisation given by Eqs. (C1)–(C5). Results are shown as kg of water per mol of total solutes as a function of equilibrium relative humidity (*RH*). (a) NaCl : $C_{12}H_{22}O_{11}$ mole ratios 1 : 0 to 1 : 1. (b) NaCl : $C_{12}H_{22}O_{11}$ mole ratios 1 : 1 to 0 : 1. Mole ratios for each curve are indicated.

coefficient of sucrose, which is obtained from Eq. (C2) using the Gibbs–Duhem relationship, is given by Eq. (C5) in Table 1.

As noted previously, both Stokes (1995) and Hu and Guo (1999) have shown that activity coefficients of NaCl in the mixture based on the osmotic coefficient measurements of Robinson et al. (1970) agree closely with values obtained directly from emf data. Predicted $NaCl_{(s)}$ and $C_{12}H_{22}O_{11(s)}$ solubilities also agree with measurements, giving confidence in the accuracy of the calculated thermodynamic properties up to saturation with respect to both solids.

Using Eqs. (C1)–(C5), we have calculated reference deliquescence curves for NaCl/ $C_{12}H_{22}O_{11}$/H_2O solutions over a range of different compositions. Unlike many probable components of atmospheric aerosols, sucrose is a solid at room temperature and thus does not take up water at all relative humidities (i.e., below its deliquescence point) as do, for example, the lower fatty acids which are liquids. The calculated deliquescence curve is shown in Fig. 1.

The two pure solids deliquesce at relative humidities of 0.75 ($NaCl_{(s)}$) and 0.845 ($C_{12}H_{22}O_{11(s)}$). (Note that throughout this work we express relative humidities as fractions rather than as percentages.) Fig. 1a shows results for NaCl : $C_{12}H_{22}O_{11}$ mole ratios 1 : 0 to 1 : 1, and Fig. 1b from 1 : 1 to 0 : 1. The general behaviour is similar to that of a mixture of two salts in that water uptake begins at a lower relative humidity for the mixture (0.63) than for either of the pure compounds. At this point, the eutectic, the mixture is simultaneously saturated with respect to both solids. An alternative view of the deliquescence properties is given in Fig. 2, which shows measured and predicted solubilities of both solids together with contours of equal relative humidity. We have not included in the deliquescence calculation the formation of the hydrate which is present in the early data compiled by Stephen and Stephen (1979b), but not found by Hu and Guo (1999).

The expressions for the mixture contributions to the total osmotic coefficient and total activity coefficients of NaCl and $C_{12}H_{22}O_{11}$, given by Eqs. (C2), (C3) and (C5), are complex and rely on an extensive set of osmotic coefficient measurements for the ternary solution. Such data are unlikely to
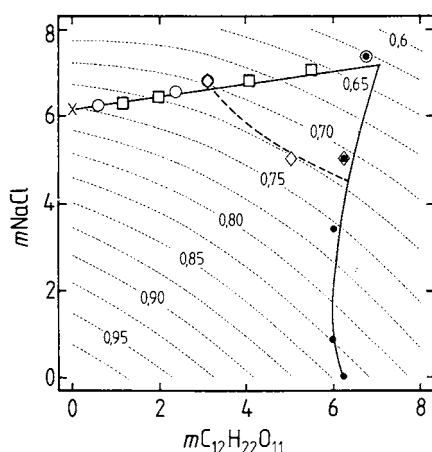
Fig. 2. Solid-phase solubilities in NaCl/$C_{12}H_{22}O_{11}$/H_2O solutions at 298.15 K: (Open circles) $NaCl_{(s)}$ (Stephen & Stephen, 1979a); (squares) $NaCl_{(s)}$ (Hu & Guo, 1999), (cross) $NaCl_{(s)}$ (Hamer & Wu, 1972); (diamond) $NaCl \cdot C_{12}H_{22}O_{11} \cdot 2H_2O_{(s)}$ (Stephen & Stephen, 1979a); (dot) $C_{12}H_{22}O_{11(s)}$ (Stephen & Stephen, 1979a). Calculated solubilities (lines) were predicted using the full model parameterisation given by Eqs. (C1)–(C5). Contours of calculated equilibrium relative humidity are also shown, from 0.60 to 0.95.

exist for soluble mixtures of typical aerosol composition. However, for the more common organic compounds "salting coefficients" may be available from gas solubility or liquid partitioning measurements. These coefficients, or the data upon which they are based, yield the term λ_{Ni} in Eqs. (7a)–(7c) for organic molecules N and perhaps also ζ_{Nca} where the relationship between $\ln(\gamma_N)$ and salt molality is nonlinear. It is instructive, therefore, to compare the deliquescence curve for NaCl/$C_{12}H_{22}O_{11}$/H_2O obtained using such a simple approach with the accurate calculation shown previously in Figs. 1 and 2.

The activity coefficient of trace $C_{12}H_{22}O_{11}$ in aqueous NaCl (γ_{Sucr}^{∞}) has been calculated using Eq. (C5). This corresponds to the activity coefficient that would be derived from gas solubility experiments in which the concentration of the organic solute in the salt solution is low. The value of $\ln(\gamma_{Sucr}^{\infty})$ is approximately linear in NaCl molality to about 2 mol kg^{-1}, and decreases at molalities above 4 mol kg^{-1}. The relationship between the two quantities is also a function of $C_{12}H_{22}O_{11}$ molality in the mixture.

Applying Eq. (9) to $\ln(\gamma_{Sucr}^{\infty})$, and setting $\lambda_{Sucr,Cl}$ to zero, we obtain Eq. (C6) in Table 1 for $\ln(\gamma_{Sucr}^{\infty})$. Assuming that Eq. (C6) applies at *all* $C_{12}H_{22}O_{11}$ molalities in the mixture, then the new mixture contributions to the total osmotic and activity coefficients ϕ''' and γ_{NaCl}''' are given by Eqs. (C7) and (C8) in Table 1, with $\gamma_{Sucr}''' = \gamma_{Sucr}^{\infty}$.

The deliquescence curve has been recalculated using Eqs. (C7) and (C8) for the mixture contributions (see Figs. 3 and 4). There is relatively little difference from that shown earlier for the accurate solution model, the main feature being a small increase in the relative humidity at the eutectic point — from about 0.63 to 0.64. The water content of the solution at this point for the 1 : 1 mixture is also very little changed from the correct value of about 0.07 kg mol^{-1}. These differences are both small compared to the uncertainties in aerosol compositions and other factors which affect typical atmospheric problems.
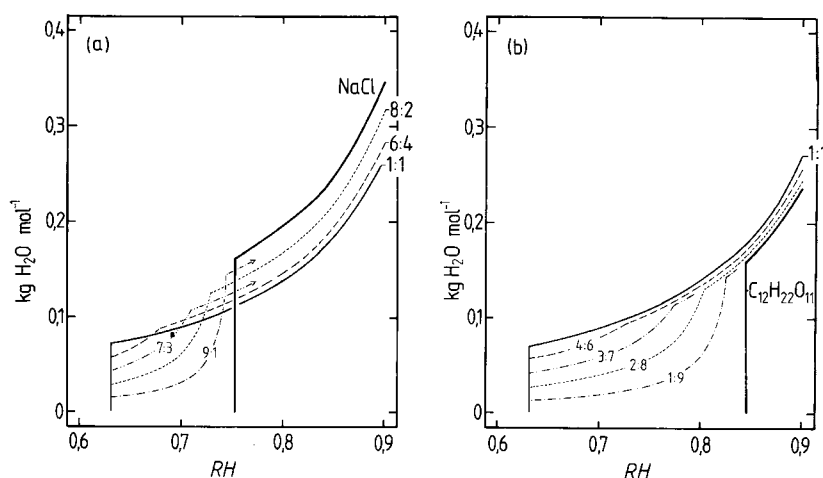
Fig. 3. Deliquescence curves for NaCl/$C_{12}H_{22}O_{11}$ mixtures at 298.15 K, calculated using the simplified model parameterisation with ion–organic contributions given by Eqs. (C7) and (C8). Results are shown as kg of water per mol of total solutes as a function of equilibrium relative humidity (*RH*). (a) NaCl:$C_{12}H_{22}O_{11}$ mole ratios 1:0 to 1:1. (b) NaCl:$C_{12}H_{22}O_{11}$ mole ratios 1:1 to 0:1. Mole ratios for each curve are indicated.
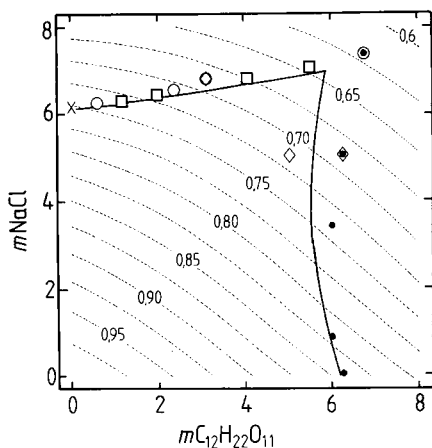

Fig. 4. Solid-phase solubilities in NaCl/$C_{12}H_{22}O_{11}$/H_2O solutions at 298.15 K. The meanings of symbols are the same as in Fig. 2. Calculated solubilities (lines) were predicted using the simplified model parameterisation with ion–organic contributions given by Eqs. (C7) and (C8). Contours of calculated equilibrium relative humidity are also shown, from 0.60 to 0.95.

It is important to consider what deliquescence properties are predicted for the simplest possible assumption: that $(\phi''' - 1)$, $\ln(\gamma'''_{Sucr})$ and $\ln(\gamma'''_{NaCl})$ are all zero, hence the properties of the mixture are estimated only from the properties of the pure solutions. For this case the uptake of water is predicted to begin at 0.675 relative humidity (0.045 greater than the true value), at which point a 1:1 mixture would have a water content of about 0.081 kg mol^{-1} compared to about 0.07 in

the accurately modelled case (Fig. 1). It is clear that the use of simple mixture contribution terms (Eqs. (C6)–(C8)) based upon the activity coefficient of trace sucrose in aqueous NaCl yields an improvement in the calculated deliquescence curve compared to using only the pure solution properties. However, the differences are not large in this example.

What would be the effect of the approximations discussed above for a volatile organic component? First, if the compound was present in only small amounts in the condensed phase relative to the ions, then salting coefficients based upon trace solubilities (Eqs. (C6)–(C8) in this example) will be essentially accurate if the relevant coefficients are known either for all ions individually or as single "lumped" λ and/or ζ parameters for the mixed salt composition of interest. We note that a single organic compound can show both salting in and salting out behaviour across the range of salts commonly found in atmospheric aerosols, thus the composition of the ionic component of an aerosol is important in determining equilibrium gas/aerosol partitioning.

The trace activity coefficient of a volatile organic compound N having the thermodynamic properties of $C_{12}H_{22}O_{11}$ in aqueous NaCl rises to a maximum of 1.23 in 4 mol kg^{-1} salt solution. Therefore, the effect of neglecting $\ln(\gamma_N'')$ in a solubility calculation would be to overestimate solubility in the condensed liquid phase by 23% for a constant gas-phase partial pressure. Where the volatile organic compound N is itself present at significant concentrations in the condensed phase then the mixture contribution to the activity coefficient is different. For example, for a solution containing 4 mol kg^{-1} NaCl and 4 mol kg^{-1} sucrose the organic–water contribution ($\ln(\gamma_{Sucr}'')$) to the logarithm of the total activity coefficient of sucrose is equal to 0.7446, and the true mixture contribution $\ln(\gamma_{Sucr}''')$ from Eq. (C5) is equal to 0.0416, giving a total activity coefficient of 2.195. The approximate mixture contribution from Eq. (C6) remains equal to 1.23 ($\ln(\gamma_{Sucr}''') = 0.207$). Hence the total activity coefficient of N is overestimated for the 4 mol kg^{-1} NaCl plus 4 mol kg^{-1} N mixture by about 18%. The sign and magnitude of such errors will vary from compound to compound, and with the composition and concentration of the liquid phase.

3.2. Letovicite/maleic acid $(C_2H_2(COOH)_2)$/water

In the previous example, the osmotic and activity coefficients for pure aqueous solutions of the organic compound were accurately known. For many organic compounds occurring in atmospheric aerosols this will not be the case. In this section we assess the effects of uncertainties in both the properties of solutions of the organic compound, and the salt effect (ion–organic interactions). The salt letovicite $((NH_4)_3H(SO_4)_2)$ is used as it more atmospherically relevant that NaCl, though also more complex as its deliquescence curve involves the formation of solid ammonium sulphate $((NH_4)_2SO_{4(s)})$ in addition to letovicite. Maleic acid (2-butenedioic acid) is a dicarboxylic acid which may occur in the atmosphere (Saxena & Hildemann, 1996) and, in common with other diacids, is likely to partition into the particulate phase. Relatively little is known concerning the thermodynamic properties of aqueous maleic acid solutions; its solubility in water is 6.9 mol kg^{-1} at 298.15 K (Stephen & Stephen, 1979b), and a deliquescence relative humidity of 0.73 has recently been measured (Brooks, pers. comm.). Osmotic coefficients of aqueous maleic acid at 298.15 K have been measured up to 3.264 mol kg^{-1} (Robinson, Smith, & Smith, 1942; Davies & Thomas, 1956). The results yield an equilibrium relative humidity (water activity) of 0.949 for a 3.0 mol kg^{-1} solution. Against this value the measured deliquescence relative humidity appears low, but the difference in the molalities is too great to allow a reliable comparison.

In the following calculations, values of ϕ' and the activity coefficient contributions of ion–water interactions (γ_i', where $i = H^+, NH_4^+, HSO_4^-, SO_4^{2-}$) are calculated using the mole fraction based model of Clegg, Brimblecombe, and Wexler (1998). The activity products of the solids $(NH_4)_3H(SO_4)_{2(s)}$ and $(NH_4)_2SO_{4(s)}$ are taken from Table 3 of the same study. Organic–water contributions to the osmotic coefficient of the mixture and to the activity coefficient of maleic acid were calculated in two different ways. First, the UNIFAC model was used, as this will be the method of choice for many atmospheric organic compounds for which no data are available. This model yields the mole fraction activity coefficients of water and maleic acid (which is assumed to be undissociated) as a function of concentration, with a reference state of the pure liquid for both components. The value of the calculated infinite dilution activity coefficient of maleic acid in water ($f_{Maleic}^{\infty''}$) is 2.358 at 298.15 K. Conversion to the infinite dilution reference state (hence $f_{Maleic}^{*''}$) and the molality basis (yielding γ_{Maleic}'') is carried out using Eq. (2b) and standard relationships (Robinson & Stokes, 1965).

Saxena and Hildemann (1997) have compared UNIFAC predictions with measured water activities for a number of organic acids. The calculated water activity of aqueous maleic acid in a saturated solution — i.e., at its deliquescence point — is 0.931 compared with the 0.73 measured by Brooks (pers. comm.). In the present calculations using UNIFAC we have accepted the deliquescence relative humidity of 0.931 in order to remain consistent with the known solubility of the acid in water. The molality of the aqueous acid in a saturated solution is 6.9 mol kg^{-1}, and its molal activity is 3.3. We note here that maleic acid has a pK_a of only 1.83 for its first dissociation (Lide, 1997). However, exploratory calculations treating this dissociation explicitly yielded only a small difference in the predicted deliquescence relative humidity.

An alternative approach to calculating organic–water contributions to osmotic and activity coefficients involves using the measured deliquescence relative humidity (0.73) and the solubility in water. A variety of one-parameter models can be based upon this information. Here we adopt the Pitzer molality based model (1991), which gives Eq. (C9) in Table 2 for the osmotic coefficient contribution ϕ''. In order to determine the value of parameter $\lambda_{Maleic,Maleic}$, $mC_2H_2(COOH)_2$ is set equal to 6.9 mol kg^{-1}, and ϕ'' is then the osmotic coefficient at the deliquescence relative humidity, given by $-\ln(0.73)/(0.0180152 \times 6.9) = 2.532$. Eq. (C9) in Table 2 then yields $\lambda_{Maleic,Maleic}$ equal to 0.2195. Eq. (C10) is the corresponding equation for the activity coefficient contribution, and yields a maleic acid activity of 145.2 in the saturated solution, a factor of 44 different from that obtained using UNIFAC, which emphasises the large differences between the two models.

Table 2
Equations for the properties of $(NH_4)_3H(SO_4)_2/C_2H_2(COOH)_2/H_2O$ mixtures

$\phi'' - 1 = mC_2H_2(COOH)_2 \cdot \lambda_{Maleic,Maleic}$	(C9)
$\ln(\gamma_{Maleic}'') = 2mC_2H_2(COOH)_2 \cdot \lambda_{Maleic,Maleic}$	(C10)
$\ln(\gamma_{SO_4}''') = 2mC_2H_2(COOH)_2 \cdot \lambda_{Maleic,SO_4}$	(C11)
$\ln(\gamma_{HSO_4}''') = 2mC_2H_2(COOH)_2 \cdot \lambda_{Maleic,SO_4}$	(C12)
$\phi''' - 1 = (1/\sum_j m_j)(2mC_2H_2(COOH)_2 \cdot (mSO_4^{2-} + mHSO_4^-) \cdot \lambda_{Maleic,SO_4})$	(C13)
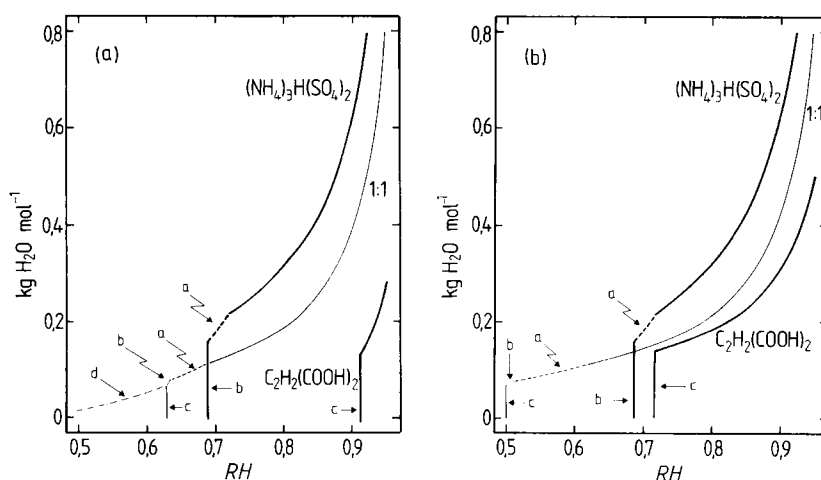
Fig. 5. Deliquescence curves for $(NH_4)_3H(SO_4)_2/C_2H_2(COOH)_2$ (letovicite/maleic acid) mixtures at 298.15 K. Results are plotted for the pure compounds, and a 1:1 molar mixture, against equilibrium relative humidity (RH). The solids are: (a) $(NH_4)_2SO_{4(s)}$; (b) $(NH_4)_3H(SO_4)_{2(s)}$; (c) $C_2H_2(COOH)_{2(s)}$. Results in plot (a) were obtained using the UNIFAC model to calculate organic–water contributions to osmotic and activity coefficients. In (b) the molality-based model given by Eqs. (C9) and (C10) was used. The dashed extension (d) to the curve for the 1:1 mixture in plot (a) assumes that the maleic acid does not precipitate to form a solid.

In Fig. 5 we show the calculated deliquescence curves for pure aqueous letovicite, pure aqueous maleic acid, and a 1:1 mole ratio mixture of the two solutes. In both sets of calculations ion–organic interaction terms were set to zero. In plot (a) the UNIFAC model was used to calculate maleic acid–water interactions, and the deliquescence relative humidity of pure maleic acid is shown as 0.91. The uptake of water per mole of maleic acid, at a given relative humidity, is less than that of letovicite by more than a factor of two. The deliquescence relative humidity of pure letovicite is 0.68, and the figure shows that, under equilibrium conditions, both ammonium sulphate and letovicite will occur as solids.

The calculated curve for the 1:1 mixture in Fig. 5a shows the expected decrease in deliquescence relative humidity relative to the pure compounds, to about 0.63 for the present model. At this relative humidity the maleic acid in the mixture dissolves, together with a fraction of the letovicite. At higher relative humidities the solution is expected to be saturated with respect to both letovicite and ammonium sulphate, and these salts take up water until a relative humidity of about 0.68 at which point the mixture becomes completely liquid. Predicted liquid water contents assuming that the maleic acid does *not* form a solid are shown as the dotted extension to the curve for the 1:1 mixture in Fig. 5a.

The deliquescence curve calculated using the alternative model of aqueous maleic acid activities (Eqs. (C9) and (C10)) is shown in Fig. 5b. Here the behaviour is qualitatively similar but the much higher uptake of water by maleic acid, reflected in the value of ϕ'', yields a significantly greater lowering of the deliquescence relative humidity predicted for the mixture — from 0.63 in the UNIFAC calculation to 0.50. Note that the solubility in water of maleic acid (6.9 mol kg^{-1}) is the same in both calculations. This quite large difference emphasises the importance of knowing

accurately the thermodynamic properties of the aqueous solutions of the organic components of the mixture. Saxena and Hildemann (1997) estimated the uncertainty in UNIFAC predictions of equilibrium RH to be about 15%. The differences between the two models of aqueous maleic acid used here are similar, about 18% in the relative humidity at the saturation molality.

Next, the variation of deliquescence relative humidity with composition is examined. A mixture of two or more soluble compounds, in *all* mole ratios, will begin to take up water at the relative humidity corresponding to that above a eutectic mixture. This is most clearly seen in Fig. 1 for $NaCl/C_{12}H_{22}O_{11}/H_2O$ mixtures, for which water uptake starts at 0.63 relative humidity. The amount of water initially absorbed is greatest for a mixture in which the two solutes are present in the eutectic ratio (about 1:1 for $NaCl/C_{12}H_{22}O_{11}$) and decreases as the mole ratio is varied away from this value in either direction. To take account of this behaviour, in the calculations that follow we consider the "total" deliquescence relative humidity (DRH^*) to be that relative humidity at which each mixture becomes fully liquid. For example, in Fig. 5a the DRH^* is 0.72 for pure letovicite and 0.68 for the 1:1 mixture. In Fig. 6 we show DRH^* as a function of mixture composition for both the UNIFAC and molality model calculations of aqueous maleic acid contributions to osmotic and activity coefficients. It is clear that in both cases the minimum DRH^* is attained for a 4:6 mole ratio of letovicite to maleic acid. For mole ratios below this value maleic acid is the first solid that precipitates as relative humidity is reduced, while for higher values it is $(NH_4)_2SO_{4(s)}$. The effect on DRH^* of uncertainties in the properties of aqueous maleic acid (indicated by the differences between the two model predictions) increases with the maleic acid content of the mixture, as expected. At the eutectic ratio the difference in DRH^* is about 13%, and for a 1:1 mole ratio it is 7%.

How do ion–organic interactions influence the deliquescence properties of the mixtures? The effects are two fold. First, "salting in" or "salting out" changes the solubilities of the dissolved solids — both organic components and salts — in the mixture. Simple salting in means an increase in the
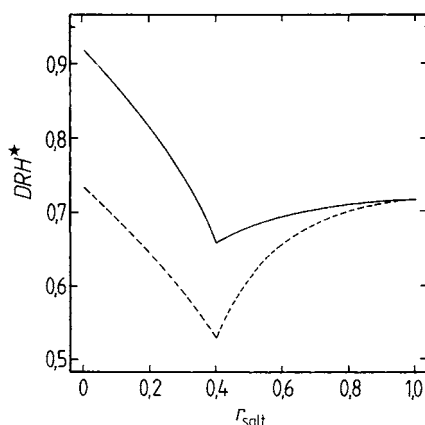

Fig. 6. Total deliquescence relative humidities (DRH^*) of $(NH_4)_3H(SO_4)_2/C_2H_2(COOH)_2$ mixtures, plotted against the molar fraction of $(NH_4)_3H(SO_4)_2$ (r_{salt}, equal to $n(NH_4)_3H(SO_4)_2/(n(NH_4)_3H(SO_4)_2 + nC_2H_2(COOH)_2)$). Results are shown for organic–water contributions to osmotic and activity coefficients calculated using both the UNIFAC model (solid line), and molality-based model (dashed line).

solubility of the organic compound, with a corresponding increase in the solubilities of one or more of the salts in the mixture, and so a lowering of the deliquescence relative humidity. Salting out of the organic compound implies the opposite effects. Second, there is the change in water activity of a solution (of fixed composition) due to the contribution of the salting coefficient to the water activity *via* ϕ'''.

The above influences on the deliquescence relative humidity of a eutectic mixture of letovicite and maleic acid have been investigated over a range of molal salting parameters $\lambda_{\text{Maleic},i}$ in the following way. The species existing in the liquid mixture are the maleic acid, H^+, NH_4^+, HSO_4^-, and SO_4^{2-}. As cation and anion salting parameters cannot be determined independently (see Eq. (9)) it is necessary to set some of the $\lambda_{\text{Maleic},i}$ to zero. For simplicity, we assume that the effects of the ion–organic interaction can be described by a single salting parameter, and that the $HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$ dissociation equilibrium is unaffected by the interaction. To achieve this, the interactions of maleic acid with H^+ and NH_4^+ are therefore set to zero, and $\lambda_{\text{Maleic},HSO_4}$ and $\lambda_{\text{Maleic},SO_4}$ assigned the same values. The ion–organic contributions to the mixture properties are therefore $\ln(\gamma_H''') = 0$, $\ln(\gamma_{NH_4}''') = 0$, and Eqs. (C11)–(C13) in Table 2 give $\ln(\gamma_{HSO_4}''')$, $\ln(\gamma_{SO_4}''')$ and $(\phi''' - 1)$.

The predicted deliquescence relative humidity above the eutectic mixture is plotted as a function of the assumed value of $\lambda_{\text{Maleic},SO_4}$ in Fig. 7. For a reasonable range of $\lambda_{\text{Maleic},SO_4}$, from about -0.2 (salting in) to $+0.2$ (salting out), the deliquescence relative humidity ranges from -0.07 to $+0.03$ compared to the base case. Except for the lowest values of $\lambda_{\text{Maleic},SO_4}$, this range is smaller than the corresponding difference between the two models of pure aqueous maleic acid (Fig. 5). This result emphasises how important the properties of the pure aqueous solutions are in determining the overall behaviour of the mixture.
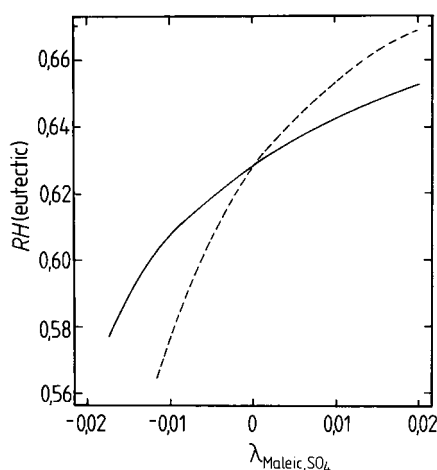

Fig. 7. Equilibrium relative humidities above an aqueous $(NH_4)_3H(SO_4)_2/C_2H_2(COOH)_2$ solution at the eutectic point, as a function of the $C_2H_2(COOH)_2 - (SO_4^{2-}, HSO_4^-)$ interaction parameter $\lambda_{\text{Maleic},SO_4}$: (Solid line) calculated for $\lambda_{\text{Maleic},SO_4}$ contributions to both osmotic and activity coefficients; (dashed line) calculated for $\lambda_{\text{Maleic},SO_4}$ contributions to the activity coefficients of solute species only.

The changes in the predicted deliquescence relative humidity can be separated into the two effects noted above. The second curve in Fig. 7 is the calculated deliquescence relative humidity where only the solubility changes of the maleic acid and the ammonium salts are taken into account — i.e., with the quantity $(\phi''' - 1)$ set to zero. It is clear that this omission approximately doubles the effect, resulting in a considerable overestimate of the change. Thus it is important that the contribution of the salting parameters to both the solute activity coefficients and water activity are calculated, where the salting parameters are known.

3.3. Sodium chloride/butanoic acid (C_3H_7COOH)/water

In extractive distillation processes involving mixed solvents, salts are often added to enhance separation. This can cause not just an increase in the vapour pressure of one of the solvents due to salting out, but also the formation of immiscible liquid phases in equilibrium with one another. Depending on the relative amounts of solvents and salt(s) initially present, the two phases can have very different compositions, with each typically being dominated by a single solvent.

It is possible that liquid/liquid phase separation occurs in internally mixed aerosols containing both organic and inorganic components and we now examine a simple example, NaCl/C_3H_7COOH/H_2O, to assess the effects on deliquescence properties. This particular system is chosen both for its simplicity and the fact that thermodynamic data are available at 298.15 K for both the binary aqueous solutions and the mixture. In the calculations that follow, values of ϕ' and $\ln(\gamma'_{NaCl})$ (i.e., the NaCl/H_2O contribution to thermodynamic properties) are taken from the review of Archer (1992) as before. The quantities ϕ'' and $\ln(\gamma''_{HBut})$ are obtained from the study of Hansen, Miller, and Christian (1955). These authors present fitted equations for the mole fraction activity coefficients of butanoic acid (f_{HBut}) and water (f_w) in their aqueous mixtures, and the equations are adopted here. Values are transformed to a molality basis using Eqs. (C14) and (C15) in Table 3. In these equations f_{HBut}^{∞} ($= 37.58$) is the activity coefficient of C_3H_7COOH at infinite dilution in water relative to a reference state of pure liquid C_3H_7COOH, x''_w is the pseudo-mole fraction of water $(1 - x''_{HBut})$, and M_w the molar mass of water. Recall that pseudo-mole fractions are calculated using the molar composition of the NaCl/C_3H_7COOH/H_2O mixture of interest, but omitting NaCl when using the above equations to determine the organic–water contributions to total osmotic and activity coefficients (Section 2).

The ion–organic contributions to the total osmotic and activity coefficients are here para-meterised using $\lambda_{HBut,Na}$ and $\zeta_{HBut,Na,Cl}$ from Eqs. (7a)–(7c), based on measurements compiled by Stephen and Stephen (1979a). The data consist of NaCl solubilities in aqueous C_3H_7COOH solutions and also the compositions of immiscible liquid phases at equilibrium — i.e., phases in which the activities of H_2O, C_3H_7COOH, and NaCl each have the same values. In mixtures in which only a single liquid phase exists, compositions are restricted to, first, a mainly aqueous region in which the mass percent of C_3H_7COOH remains below about 1.5, and a chiefly acid region (mass% of C_3H_7COOH greater than 89) in which the concentration of salt is very small, less than about 0.12%. Compositions of the two-phase liquid system are shown in Fig. 8. In plot (a) the mass% of C_3H_7COOH in both liquid phases is plotted against the mass% of NaCl in the aqueous layer. Thus the circles give the measured compositions of the aqueous layer, and the dots give the corresponding mass% of C_3H_7COOH in the organic layer. The mass% C_3H_7COOH in the organic layer is shown in Fig. 8(b) as a function of NaCl mass%.
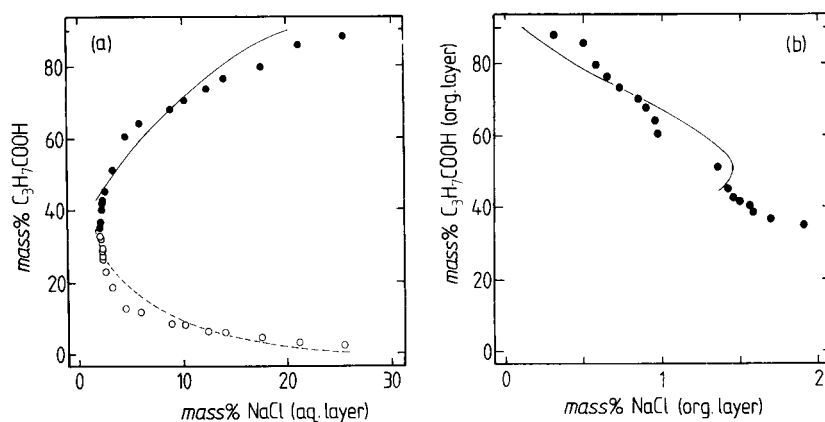
Fig. 8. Compositions of immiscible $NaCl/C_3H_7COOH/H_2O$ phases in equilibrium with each other. (a) Concentrations (mass%) of C_3H_7COOH in both phases plotted against the concentration of NaCl in the aqueous layer: (Circle) C_3H_7COOH in the aqueous layer; (dot) C_3H_7COOH in the organic layer; (lines) calculated using the model described in Section 3. (b) Concentrations of C_3H_7COOH in the mainly organic layer plotted against NaCl concentration in the organic layer. The line was calculated using the model described in Section 3. Data are from the compilation of Stephen and Stephen (1979a).

Table 3
Equations for the properties of $NaCl/C_3H_7COOH/H_2O$ mixtures

$\ln(\gamma''_{HBut}) = \ln(f''_{HBut}) - \ln(f''^{\infty}_{HBut}) + \ln(x''_w)$	(C14)
$\phi'' = -[\ln(f''_w) + \ln(x''_w)]/(M_w mC_3H_7COOH)$	(C15)
$\phi''' - 1 = [2/(2mNaCl + mC_3H_7COOH)](mNaCl \cdot mC_3H_7COOH \cdot \lambda_{HBut,Na}$ $+ mNaCl^2 \cdot mC_3H_7COOH \cdot \zeta_{HBut,Na,Cl})$	(C16)
$\ln(\gamma'''_{NaCl}) = 0.5(\ln(\gamma'''_{Na}) + \ln(\gamma'''_{Cl})$ $= mC_3H_7COOH \cdot \lambda_{HBut,Na} + mNaCl \cdot mC_3H_7COOH \cdot \zeta_{HBut,Na,Cl}$	(C17)
$\ln(\gamma'''_{HBut}) = 2mNaCl \cdot \lambda_{HBut,Na} + mNaCl^2 \cdot \zeta_{HBut,Na,Cl}$	(C18)

The model was fitted using parameters $\lambda_{HBut,Na}$ and $\zeta_{HBut,Na,Cl}$ to give expressions for the mixture contributions to osmotic and activity coefficients given by Eqs. (C16)–(C18) in Table 3. These equations apply, as do those for the $NaCl/H_2O$ and C_3H_7COOH/H_2O contributions, to activities in both the aqueous and acid phases. The fit of the equations was carried out using the two-phase composition data, but restricted to C_3H_7COOH molalities below 40 mol kg^{-1} in the organic layer. The fit yielded $\lambda_{HBut,Na}$ equal to 0.01518, and $\zeta_{HBut,Na,Cl}$ equal to 0.08714. Calculated equilibrium phase compositions for this result are plotted in Fig. 8. The errors — which are most significant where the compositions of the two phases are quite similar to one another (near 35 mass% C_3H_7COOH) — are larger than typically found when fitting vapour pressure or salt solubility data. The liquid phase separation problem is quite a severe test of models; in the present case the activity coefficients of all three components need to be accurately predicted over the very wide range of compositions covered by both phases.
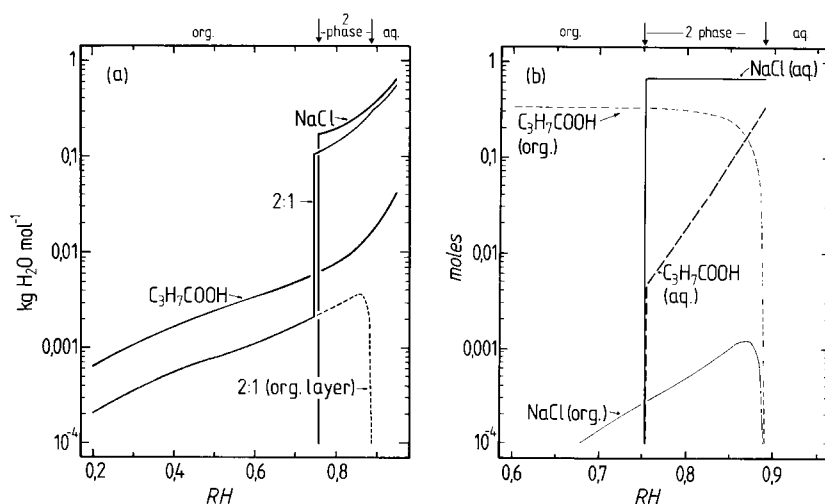
Fig. 9. Deliquescence curves for a 2:1 mole ratio NaCl/C_3H_7COOH mixture at 298.15 K. (a) Water uptake (kg per mol of total NaCl + C_3H_7COOH) plotted against relative humidity (RH): (Solid line (labelled 2:1)) total water content for both liquid phases; (dashed line) water content of the mainly organic phase only. Curves for 1 mol of both pure NaCl and pure C_3H_7COOH (heavy solid lines) are also shown. The single and two phase regions are marked on the upper horizontal axis. (b) Amounts of dissolved NaCl and C_3H_7COOH (moles) in each phase for the 2:1 mixture, plotted against RH. Lines: (full solid) NaCl in the aqueous phase; (fine solid) NaCl in the organic phase; (full dashed) C_3H_7COOH in the aqueous phase; (fine dashed) C_3H_7COOH in the organic phase. The single and two phase regions are marked on the upper horizontal axis.

Using the model equations above we have calculated the deliquescence curve of a 2:1 NaCl:C_3H_7COOH mixture; see Fig. 9. Both the total amount of water, and the water content of the second (mainly organic acid) phase that exists over a part of the relative humidity range, are shown in Fig. 9a. Curves for 1 mol of NaCl, and 1 mol of C_3H_7COOH, are also shown. The numbers of moles of the two solutes in each phase are plotted in Fig. 9b. Beginning at a relative humidity of 0.95 in Fig. 9a the water content decreases with falling relative humidity to an inflexion point at 0.885 relative humidity where the formation of the mainly organic second phase occurs. This second phase, although it contains most of the C_3H_7COOH for relative humidities less than about 0.77, retains very little water. At 0.75 relative humidity both liquid layers become saturated with respect to NaCl$_{(s)}$. We note that this deliquescence relative humidity hardly differs from that of a pure aqueous NaCl solution. Considering the composition of the aqueous phase, this can be attributed to the fact that the concentration of C_3H_7COOH in that phase is very small as most (a factor of 50 more) resides in the organic phase.

As relative humidity is reduced below 0.75 the aqueous phase disappears leaving only a single liquid phase that contains all of the C_3H_7COOH present (0.3333 mol) and a small amount of dissolved NaCl (less than 1/1000 of the total) which is in equilibrium with solid NaCl$_{(s)}$. Although the C_3H_7COOH remains liquid at all relative humidities below 0.75, the amount of water retained is very small, less than 2×10^{-3} kg compared with about 0.1 kg at the deliquescence point of NaCl$_{(s)}$.

Despite the relatively complex behaviour of this NaCl/C_3H_7COOH/H_2O mixture and the fact that it retains a liquid, water soluble, element at all relative humidities, the overall water uptake

differs little from that of a system containing only NaCl. One reason for this is that, for a given relative humidity, C_3H_7COOH takes up very little water compared to NaCl or indeed any other salt above its deliquescence point. For example, at equilibrium with 0.95 relative humidity the water content of aqueous C_3H_7COOH is about 0.045 kg mol^{-1}, compared with almost 0.7 kg mol^{-1} for an NaCl solution. A second factor is that the separation into two liquid phases removes most of the C_3H_7COOH from the aqueous phase (which contains most of the salt). Consequently the relative humidity of deliquescence of NaCl in the mixture is decreased only slightly — much less than would have been the case if only a single liquid phase existed.

The present example, in which quite complex phase relations result in rather simple deliquescence properties, may be a special case. In atmospheric systems many more compounds are likely to be present, and it remains unclear to what extent, if at all, phase separation will occur in the aerosol. However, a few things can be said. The most general condition that must be satisfied for liquid/liquid phase separation to occur is that the activity of each component must be the same in both phases. In the example studied here an indication of the likelihood of phase separation occurring can be gained by comparing the variation of water activity of aqueous NaCl and aqueous butanoic acid solutions with concentration (see Fig. 10). The water activity of aqueous NaCl decreases comparatively steeply with concentration, and a 6 mol kg^{-1} (0.0975 mol fraction) saturated solution of NaCl has a water activity of 0.75 at 298.15 K. This is not the case for aqueous butanoic acid, for which the same water activity is reached only at 172 mol kg^{-1} (0.756 mol fraction). It is clear, intuitively, that a solution concentrated with respect to NaCl, but dilute in butanoic acid, could have the same water activity as one concentrated with respect to butanoic acid but dilute with respect to NaCl. While this is not the only criterion for phase separation it does
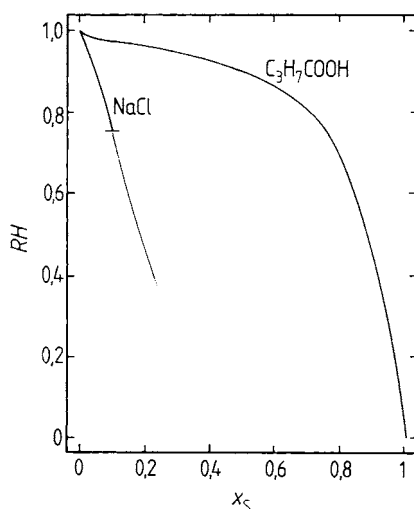

Fig. 10. Equilibrium relative humidity (RH) above aqueous NaCl and C_3H_7COOH solutions at 298.15 K, as a function of mole fraction x_s, where s = NaCl or C_3H_7COOH. For this plot mole fraction is defined as $x_s = n_s/(n_s + n_w)$ where n_w is the number of moles of water. Aqueous NaCl solutions become saturated at 298.15 K at about 0.75 RH (marked by the break in the curve). The extension to lower RH is based on the electrodynamic balance measurements of Tang, Munkelwitz, and Wang (1986).

indicate the kind of thermodynamic behaviour required of the aqueous organic compound for it to occur.

4. Discussion and summary

There are two key elements to the modelling approach used here. First, the ion–water, organic–water, and ion–organic contributions to osmotic and activity coefficients are calculated independently. In particular, calculations of the ion–water and organic–water terms each require only the solution compositions with respect to the two groups of solutes (ions and uncharged organic molecules, respectively). Thus, in the examples presented here, the NaCl–water contributions to the osmotic coefficients of the $NaCl/C_{12}H_{22}O_{11}/H_2O$ and $NaCl/C_3H_7COOH/H_2O$ solutions, and the activity coefficients γ_{Na} and γ_{Cl}, can be derived from any model that yields the thermodynamic properties of pure aqueous NaCl. The approach generalises to more complex solutions; for soluble aerosols containing several ions and organic solutes the ion–water contributions can be calculated with an electrolyte activity coefficient model, and similarly the organic–water contributions with a model such as UNIFAC.

The second important feature is the use of expressions for ion–organic contributions to osmotic and activity coefficients derived from a single expression for their contribution to the excess Gibbs energy (Eqs. (8) and (9)). This ensures thermodynamic consistency of these contributions to the activity coefficients of all solute species and to the water activity.

If the ion–organic parameters are unknown (and consequently set to zero), then the activity coefficients calculated for ions and organic molecules will be the same as those that would be obtained for separate ion–water and organic–water solutions at the same species molalities as occuring in the mixture. However, the osmotic coefficient of the mixture is a function of the molalities of all solutes. This is why, for example, the calculated relative humidity above an $NaCl/C_{12}H_{22}O_{11}/H_2O$ solution at the eutectic point is correctly predicted to be lower than the relative humidities above saturated pure aqueous NaCl and $C_{12}H_{22}O_{11}$ solutions even when the ion–organic parameters in the model are set to zero.

In the examples presented here we have shown, first, how the modelling approach is applied to a system for which there are comprehensive data ($NaCl/C_{12}H_{22}O_{11}/H_2O$), and that a simple approximation of the ion–organic interaction (that the activity coefficient of $C_{12}H_{22}O_{11}$ in the mixture is equal to its "trace" value in aqueous NaCl for all $C_{12}H_{22}O_{11}$ molalities) predicts the deliquescence curve satisfactorily. This approximation is typical of the what is likely to be necessary in atmospheric studies where data for many of the compounds of interest are limited.

The thermodynamic properties of aqueous solutions of organic compounds are quite poorly known compared to those of electrolytes. In many applications it is likely that UNIFAC will be used, despite the fact that the model is generally unsuited to the structurally complex, highly oxygenated, compounds occurring in atmospheric aerosols. In calculations of the deliquescence properties of $(NH_4)_3H(SO_4)_2/C_2H_2(COOH)_2/H_2O$ mixtures we have compared results using both UNIFAC and another simple model expression (based upon a measurement of the deliquescence relative humidity of solid $C_2H_2(COOH)_{2(s)}$). Differences in the predicted relative humidity of the eutectic mixture of 13% emphasise the importance of an accurate knowledge of the properties of aqueous solutions of the organic components of the mixture.

It is instructive to compare measured activities in aqueous solutions of the C-4 acids with those predicted using UNIFAC. As previously noted, UNIFAC yields a water activity of a saturated solution of maleic acid (0.93 at 6.9 mol kg^{-1}) that is much higher than the measured value of 0.73 for the deliquescence relative humidity. The error is in the same direction for malic acid, 2-hydroxy-butanedioic acid, which has a solubility in water of 10.3 mol kg^{-1} at 298.15 K. The water activity of a saturated solution is about 0.79 (Saxena & Hildemann, 1997), compared to 0.86 predicted by UNIFAC. Osmotic coefficients of both aqueous malic acid (to 6.42 mol kg^{-1}) and maleic acid (to 3.264 mol kg^{-1}) have been measured at 298.15 K (Robinson et al., 1942; Davies & Thomas, 1956) and comparisons of UNIFAC predictions with the data confirm the errors noted above, at least for malic acid. By contrast, UNIFAC tends to predict water activities that are too low for butanoic acid compared to the measurements of Hansen et al. (1955), suggesting that the errors are associated with there being two carboxylic acid groups on the organic molecule. It should be remembered that some lower carboxylic acids, including acetic acid and methacrylic acid, tend to dimerise in aqueous solution. Such behaviour would also affect the thermodynamic properties of the solutions and is not taken into account directly by UNIFAC.

Our approach is necessarily based upon the assumption of a single solvent (water) in which ions and organic molecules are dissolved. (This is true even for the final example in Section 3 where water is treated as the solvent for both liquid phases.) The equations for ion–organic contributions to osmotic and activity coefficients are consequently expressed on a molality basis. For low to moderate molalities these expressions (from the model of Pitzer) are well proven. However, results are likely to be less good for systems at low relative humidities where solute molalities may be very high. As a test, and to investigate the possible influence of liquid/liquid phase separation on deliquescence in solutions with a large organic content, we applied the model to the mixture NaCl/C_3H_7COOH/H_2O. The result, using two parameters for ion–organic interactions, was able to predict phase separation in this simple system for most compositions. The second (largely organic) phase was found to contain very little water, resulting in a deliquescence curve for the mixture that differed only slightly from that for pure aqueous NaCl.

We have not discussed the application of the present modelling approach to the vapour–liquid equilibrium of organic compounds, or to organic compounds that will dissociate in aqueous aerosol solutions to form ions (moderately strong acids, for example). The organic ions would have to be treated as individual solute species within the same model used for the inorganic ions to calculate osmotic and activity coefficient contributions γ' and ϕ'. As there are relatively few data available, simplifying assumptions would need to be made, possibly using analogies with inorganic ions to set model parameters. The present approach applies to vapour–liquid equilibrium without alteration, as the ion–organic interactions contribute to the value of the activity coefficient of the organic or other volatile species in equilibrium with the gas phase. It is emphasised that ion–organic contributions are completely general in that values determined, for example, from salt solubilities in an aqueous solution of an organic compound will also correctly predict the effect of the salt on the equilibrium of the dissolved organic compound with the vapour phase. This derives from the self-consistency of Eqs. (6) and (7).

The modelling approach used here is not intended to be applied to liquid systems containing both salts and soluble organic compounds at very low relative humidities. Such liquids may be better treated as mixed solvent systems, and ion–organic contributions to thermodynamic properties from Eqs. (6) and (7) would be unlikely to be accurate over the full range of compositions and

concentrations. However, there are many other uncertainties affecting the interactions of water and the organic components of the system which affect both liquid/solid and liquid/vapour equilibrium. It was shown in the $(NH_4)_3H(SO_4)_2/C_2H_2(COOH)_2/H_2O$ example in Section 3 that such uncertainties — largely caused by a lack of data — remain even in the systems considered here. Consequently only simple approaches to modelling ion–organic effects on thermodynamic properties of mixed inorganic/organic soluble aerosols, based on a minimal set of parameters, seem justified at present.

Acknowledgements

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